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Electrochemical Capacitor Properties of NiO in Ionic Liquids

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The electrochemical capacitor properties of dip-coated NiO/Ni were studied in six different ionic liquids and compared with a typical nonaqueous electrolyte and an alkaline electrolyte. A 3 V working potential for the ionic liquids leads to a larger energy density when compared to KOH electrolyte, with the highest energy density obtained in EMI-BF_4.

Metal oxides have been studied as potential candidates as electrodes for electrochemical capacitors. Various oxides have been proposed so far, including oxides of Ru, Ir, V, Mn, Mo, and Ni.[1] As a light and abundant material, nickel oxide is a potential candidate, showing electrical double layer capacitor like behavior between 0.87–1.27 V vs. RHE in alkaline electrolytes.[2] Specific capacitance of 200–300 $F\,g^{-1}$ has been reported,[2,3] which is comparable to commercial activated carbon electrodes. Although the high capacitance is inspiring, the narrow electrochemical window (ca. 0.5 V) limits the use of NiO electrodes for many applications, as the energy density of a capacitor is $1/2CV^2$. Thus, it would be beneficial if the electrochemical potential range could be widened.

Ionic liquids have attracted increased interest as a new electrolyte system with high conductivity and wide electrochemical window. Only a few studies have been conducted so far regarding the capacitive behavior of oxide electrodes in ionic liquids. RuO_2 electrodes have been reported to exhibit lower specific capacitance in ionic liquids compared to sulfuric acid.[4,5] A study using a nickel-based rare earth oxide prepared by oxidation of a nickel-based misch metal reports capacitance of 360 $F\,g^{-1}$ with a 2 V electrochemical window in 1-butyl-3-methylimidazolium hexafluorophosphate.[6] Here, we report the capacitive properties of NiO in various ionic liquids and compare them to the behavior in alkaline and nonaqueous electrolytes.

NiO electrodes were prepared by dip-coating following literature procedures.[2] $Ni(CH_3COO)_2\cdot4H_2O$ (Aldrich) was dissolved in distilled water, and magnetically stirred for 3 days under ambient conditions to obtain a sol. The green precipitate was centrifugally collected and dispersed in distilled water. A Ni plate ($1 \times 1\,cm^2$, 0.1 mm thick) was dipped into this dispersion at a rate of 0.1 $cm\,s^{-1}$. After drying, the electrode was heat-treated at 300 °C in air to obtain NiO/Ni. The weight of the coating, typically 0.2 $mg\,cm^{-2}$, was measured using a microbalance (AEG-45SM, Shimadzu).

A three electrode cell was employed for electrochemical characterization. The counter electrode was Pt and the reference electrode was a Ag/Ag^+ (BAS). All electrochemical measurements were conducted in a N_2-filled dry box (dew point < -90 °C). The ionic liquids used were 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF_4), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMI-TFMS), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI-TFSI), *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium tetrafluoroborate (DEME-BF_4), *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI), and 1-butyl-3-methyl-imidazolium hexafluorophosphate (BMI-PF_6). 1 M tetraethylammonium tetrafluoroborate/propylene carbonate (TEA-BF_4/PC) was used as the nonaqueous electrolyte. 1 M KOH was also studied as the alkaline electrolyte. All reagents were used as-received. X-ray diffraction (XRD) was conducted with a Rigaku RINT2500HF/PC, and a Hitachi S-5000 was used for scanning electron microscopy (SEM).

SEM images of the surface of the NiO/Ni electrode revealed fine nanoparticles constituting a mud-crack-like porous network (Figure S1).[11] The XRD pattern of the prepared NiO/Ni electrode reveals a broad peak at $2\theta = 38°$, which can be indexed as the (111) reflection of NiO (Figure S2).[11] The particle size estimated from this peak was ca. 4 nm, in accordance with the SEM images.

The cyclic voltammogram of NiO/Ni in 1 M KOH is typical of a polarizable electrode, characterized by a rectangularly shaped voltammogram with no appreciable faradaic process, which indicates that the charge storage is dominated by the electrical double-layer charging (Figure S3).[11] The specific capacitance was 100 $F\,g^{-1}$ at 2 $mV\,s^{-1}$ and decreased to 60 $F\,g^{-1}$ at 500 $mV\,s^{-1}$. The specific capacitance values are in accordance with reported literature values[1,7,8] and are comparable to porous carbons under similar experimental conditions. However, the energy density, 8 $kJ\,kg^{-1}$, is considerably low due to the narrow potential window of 0.4 V.

Cyclic voltammogram of NiO/Ni in 1 M TEA-BF_4/PC at 2 $mV\,s^{-1}$ is shown in Figure 1a. The voltammograms reveal no evidence of redox reactions, typical of a non-Faradaic ideally polarizable electrode. The capacitance is 19 $F\,g^{-1}$ at 2 $mV\,s^{-1}$, which is much lower than the capacitance in 1 M KOH but higher than the capacitance of 8 $F\,g^{-1}$ reported for RuO_2 in 1 M TEA-BF_4/PC.[5] Although the capacitance is low compared to 1 M KOH, the 2.5 V potential window results in a sevenfold greater energy density of 58 $kJ\,kg^{-1}$.

Voltammograms of NiO/Ni in six different ionic liquids are shown in Figures 1b–1g. The specific capacitance and energy density are summarized in Table S1.[11] The specific capacitance in ionic liquids ranged from 12 to 33 $F\,g^{-1}$, with EMI-BF_4 affording the highest capacitance. These values are considerably higher than the reported 6.5 $F\,g^{-1}$ for RuO_2 in the same electrolyte EMI-BF_4.[4] Redox peaks suggestive of any faradaic contribution from the cation or the anion was not observed, thus we believe that the capacitive behavior for NiO in organic electrolytes is mainly due to electrical double layer charging. It should be noted that redox peaks due to faradaic reactions are clearly observed when the upper potential limit is increased to

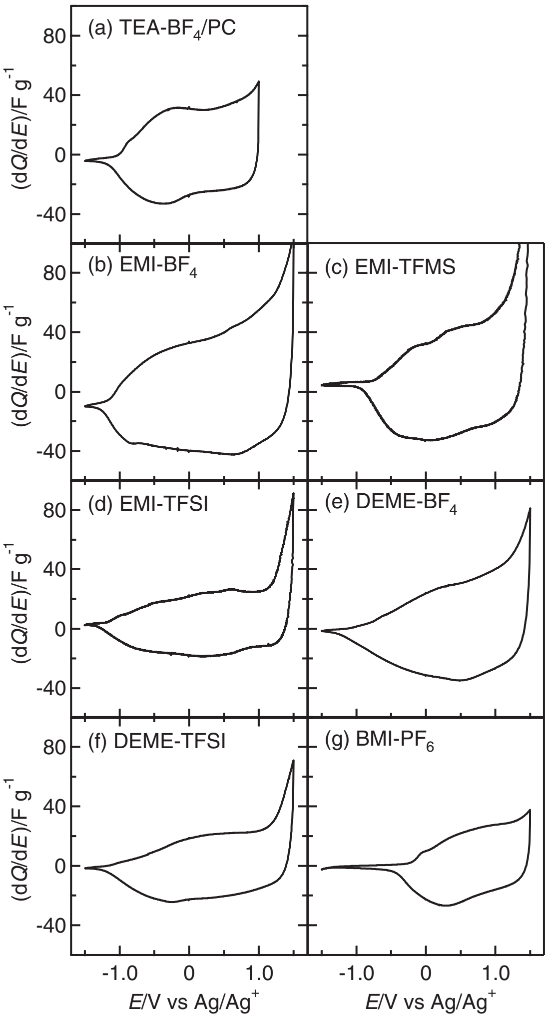

Figure 1. Cyclic voltammograms of NiO/Ni in various electrolytes at 2 mV s^{-1}.

ca. 1.6 vs. RHE in 1 M KOH.[11] In addition, using the specific surface area of 110 m^2 g^{-1} measured by N_2 sorption studies for nonsupported NiO obtained by heat treatment of the dried sol, specific capacitance per unit surface area of 11–30 µF cm^{-2} is obtained, which is close to values for most carbonaceous materials. These results are in support of the conclusion that the capacitive behavior for NiO in organic electrolytes is due to non-faradaic reactions.

The sharp rise in current observed in the high-potential region may be due to residual water in the electrolyte. The 3 V potential window results in a large energy density. Although the specific capacitance in EMI-BF_4 was a mere 1/3 of that in 1 M KOH, the energy density obtained in EMI-BF_4 was almost 20 times higher due to the 3 V window applicable in EMI-BF_4 as compared to the 0.4 V window for KOH. The largest energy density obtained in this work was 150 kJ kg^{-1} in EMI-BF_4. The specific capacitance obtained for NiO/Ni in various ionic liquids can be discussed based on the size of the cations and anions. The specific capacitance increases with the decrease in the ionic radius of the anion or the cation; the combination of EMI$^+$ and BF_4^- giving the largest specific capacitance while ionic liquids based on comparatively larger DEME$^+$ and TFSI$^-$ results in smaller capacitance (Figure 2). This trend can be compared to work on carbon-based electrical double layer capacitors where the capacitance increases with the decrease in the size of the ions.[9,10]

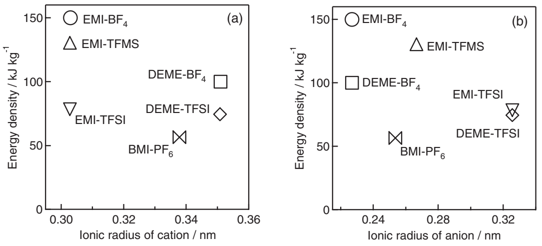

Figure 2. The energy density as a function of the ionic radius of the (a) cation and (b) anion.

In conclusion, the capacitive behavior of dip-coated NiO/Ni was studied in various aqueous and nonaqueous electrolytes. Within the nonaqueous electrolytes studied, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF_4) afforded the highest specific capacitance of 33 F g^{-1} and energy density of 150 kJ kg^{-1}. The energy density was 20 times higher than 1 M KOH electrolyte. The charge storage behavior in nonaqueous electrolytes is suggested to arise mainly from electrical double layer charging. As a consequence, the charge storage capability in nonaqueous electrolytes was strongly dependent on the size of the ions.

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